RE-ORDER NO. 63-685

November 20, 1963

Interim Report No. 1

STERILIZABLE SILVER-ZINC BATTERY

JPL [redacted] 950364

Subcontracted under NASA Contract NAS7-100

Delco-Remy Div[redacted]
General Motors Corporation
Anderson, Indiana

17 Prepared for JPL

Prepared by:

R. S. Bogner
Project Leader

Approved by:

J. J. Lander, Director
Electrochemical Research
Department

RE-ORDER No. 63-695

TABLE OF CONTENTS

RE-ORDER No. 63-675

LIST OF FIGURES

LIST OF TABLES

3

RE-ORDER No. 63-685

ABSTRACT

The various cell components were sterilized at 145°C for 36 hours to determine their ability to withstand sterilization and the effect of their degradation products on cell performance. New types of separators and case materials were investigated. Various methods of sealing nylon were tested.

Both positive and negative plates were capable of withstanding the sterilization requirement. Removal of the polyvinyl alcohol from the negative plates decreased the pressure build up during sterilization and has not resulted in a significant loss of cell capacity in 50 cycles.

The fibrous sausage casing separator materials are degraded beyond use during sterilization, and the degradation products cause immediate cell failure.

The methacrylic and acrylic acid grafts on teflon and cross-linked high density polyethylene separators prepared by R.A.I. survived sterilization. Cells containing the sterilized teflon base separators failed early due to shorts, as did their controls. Cells containing sterilized polyethylene base separators have passed 26 cycles and are still cycling.

Nylon degradation products did not affect cell performance. Of the three nylons tested, Zytel 38 was not as prone to attack as Zytels 101 and 121 in KOH at 145°C for 48 hours. Phenol was superior to epoxy, nylon-bodied calcium chloride-ethanol, and heat for the case-to-cover seal for nylon cases. Effective seals on glass-filled Zytel 38 were not attained and are still under investigation.

Evaluation of possible new case materials resulted in two which can be injection molded with present equipment. They are Celcon and Penton.

Molds for a new case and cover design are under construction for continuation of the battery testing portion of the program. The new design is applicable to either a heat or solvent seal and should be stronger than the present design.

I. Introduction

This is an interim report covering the testing of secondary silver-zinc cell components to determine their ability to withstand a sterilization temperature of 145°C for 36 hours. In a previous investigation[1] it was found that silver-zinc cells sterilized at 145°C yielded less than 50% of their rated capacity. The voltage characteristics were about 0.10 to 0.15 volts below that of a normal cell. The loss of cell performance was suspected to be due to the degradation products of the separators and/or case material.

The present investigation was initiated to determine which cell components would survive the sterilization environment and to find replacements for the components that failed or were detrimental to cell performance. All cells tested in this program were rated at 25 a.h. at the three-hour rate.

II. Cell Component Evaluation

The general method of approach to evaluate the various cell components was to sterilize each component individually in sealed stainless steel containers equipped with pressure gauges. All components were sterilized at 145° for 36 hours in an appropriate quantity of 40% potassium hydroxide solution. The "liquor" from the sterilized cell components was used to activate cells of standard construction. Standard construction, as referred to in this work, consists of cells containing six positive and seven negative plates made as described in the June 10, 1962 Report under JPL Contract Nr. 950177. The separators consisted of one layer of dynel and three layers of fibrous sausage casing. The cells are rated to yield 25 a.h. when discharged at the three-hour rate at room temperature. The effect of the degradation products on cell performance was determined by cycling the cells at the three-hour rate at room temperature.

The sterilization containers were formed from 1/16 inch stainless steel sheet and welded across the bottom and up two sides. After welding, the cans were leak checked with a Veco leak detector. The material to be sterilized

(1) R. S. Bogner, Final Report under JPL Cont. Nr. 950177, Oct. 15, 1962

was placed in the container and the cover was welded on. The cans were again leak checked. The covers had a stainless steel fitting welded to them for attachment of a pressure gauge. Marshall Town pressure gauges calibrated from zero to 100 psi were used to determine pressure. High purity silver goop was used to seal the threads. Figure 1 shows an assembled sterilization container.

A. Active Material

In order to continue this program, it had to be determined whether or not the active plate materials were capable of surviving the sterilization requirement. The following tests proved that both the positive and negative plates will survive sterilization, as was expected.

1. Positive Material

Twenty positive plates (unformed) were sterilized in stainless steel cans. After sterilization the plates were washed and dried. Three cells were assembled combining the sterilized positive plates with regular standard negative plates and separators. The cells were activated with 85 ml of fresh 40% potassium hydroxide and cycled at the three-hour rate.

Table 1 shows cell capacity and cycle life of the cells. To date cells containing sterilized positive plates have passed 49 cycles. There is no indication that the positive plates were adversely affected by sterilization. The voltages on charge and discharge are comparable to the control cells.

2. Negative Material

Negative plates were made by the standard procedure and sterilized in the stainless steel containers. The plates survived sterilization with little apparent degradation; however, the viscon paper wrap was somewhat degraded. The negative plates could not be washed and dried because the zinc oxide would wash away.

The sterilized negative plates were assembled with standard separators and positive plates to make three cells. The cells were activated with 85 ml of fresh 40% potassium hydroxide and cycled at the three-hour rate. To date the cells have passed 49 cycles, as shown in Table 1, and they are giving good capacities. There is no indication that the plates were adversely affected by the sterilization procedure.

From Table 2 it will be noted that the maximum pressure reached during sterilization was in excess of 100 psig. Because of this high pressure, it was decided to try two additional experiments to determine what consituents of the plates produced the pressure. In one test, negative plates were built by the standard method except water was used in place of the polyvinyl alcohol, and these plates were sterilized. For the second test a mixture of the active material (ZnO-HgO) only was sterilized.

As noted in Table 2 the negative plates without PVA produced a maximum pressure of 62 psig while the active material mix without PVA produced a pressure of only 32 psig. From these results, it is concluded that both the PVA binder and the viscon paper wrap on the negative plates contribute to an excess pressure build up.

Standard separators and positive plates were assembled with the sterilized negative plates without the PVA to build three cells. The cells were filled with electrolyte and cycled at the three-hour rate. To date the cells have passed 36 cycles with capacities and voltages comparable to the control cells. This test indicates that it should be possible to use negative plates that do not contain PVA, and this should greatly enhance the possibility of getting cells through sterilization without bursting the case. The PVA was originally introduced into the plates because it was found to increase cycle life on the A.S.D. program[2]. The cycle was a continuous two-hour cycle (35 minutes discharge - 85 minutes charge) at about 25% depth.

Three cells were also assembled using negative plates made from

(2) J. A. Keralla, "Report of Testing on Sealed Silver Oxide-Zinc Secondary Cells," Contract Nr. AF33(600)-41600, October 25, 1961.

the sterilized zinc-oxide material mix. After sterilization, the material was washed, dried, pulverized and made into plates. No PVA was used, but the Viscon paper wrap was used. The cells made from these plates have passed 36 cycles and are performing satisfactorily thus far.

B. Separator Materials

1. Present Separators

Fibrous sausage casing (F.S.C.), Dynel and Permion 600 separator materials were sterilized in separate containers. The quantity of each material sterilized was equivalent to the amount needed to build three cells. Approximately 300 ml of 40% potassium hydroxide was used for each material. The pressures developed by each material during sterilization are recorded in Table 2. The maximum pressures were: F.S.C., 54 psig; Dynel, 55 psig; Permion 600, 57 psig.

The liquor from the F.S.C. after sterilization was colored dark amber and its odor suggested the presence of an ester. The material was quite fragile and could not be used to build cells.

Three cells of standard separator construction were filled with 85 ml of the liquor from the F.S.C. and cycled a few times. These cells yielded capacities of four to nine ampere hours, and their voltages were about 0.3 volts below normal. The discharge curve is shown in Figure 2 and is similar to the curve of cells sterilized at 145° during the previous program (ref. 1). It is concluded that the F.S.C. separator definitely must be replaced and was probably the prime cause of cell failure as far as electrochemical capabilities are concerned.

The liquor from Dynel was light amber and smelled strongly of ammonia. The Dynel was removed from the can in one piece, but it was very easily torn and more fragile than the F.S.C. Three cells of standard construction were filled with 85 ml of the liquor from the sterilized dynel and cycled at the three-hour rate. To date these cells have passed 54 cycles and are yielding capacities comparable to the control cells. On the other hand, the discharge curve of the Dynel cells shown in Figure 2 does not exhibit any divalent silver oxide voltage. It is recalled that the divalent silver oxide voltage was also absent in cells sterilized at 125°C.

The liquor from Permion 600 was dark amber and smelled strongly of ammonia along with another odor. The Permion material was not as easily torn as F.S.C. but it was still too fragile to use to build cells. Three cells of standard construction were filled with 85 ml of the liquor from sterilized Permion 600 and cycled at the three-hour rate. The cells gave normal discharge curves, but their capacities were somewh t lower than the controls. The average initial capacity of the cells was about twenty ampere hours and gradually dropped to thirteen ampere hours at 27 cycles when the cells were removed from the test. From the results of this test, it is concluded that Permion 600 should not be used in an attempt to sterilize cells at 145°C.

Since the odor of ammonia was detected in the liquor from Dynel and Permion 600, a test was made to determine the effect of ammonia. A cell was filled with a solution of 40 ml of concentrated ammonium hydroxide and 45 ml of 40% potassium hydroxide. During charge the cell voltage never got above 1.50 volts and the cell self-discharged over night, thus demonstrating the harmful effect of ammonia in large concentrations.

2. New Separators

The following separator materials were prepared by Radiation Applications Incorporated and supplied to Delco-Remy for evaluation:

RAI Notebook No.	Separator Material
155-79-3	Teflon (TFE), acrylic acid graft
155-85	Teflon (TFE), methacrylic acid graft
155-79-5	Teflon (TFE), sulfonated styrene graft
157-87	Crosslinked (30M rads) high density polyethylene, acrylic acid graft
157-92	Crosslinked (30M rads) high density polyethylene, methacrylic acid graft.

RE-ORDER No. 63-685

Approximately fifteen square feet of each material was supplied. Half of each separator sample was sterilized at 145°C for 36 hours in the containers filled with 200 ml of 40% potassium hydroxide. The pressures developed during sterilization were about equal to the pressures calculated from the partial pressures of air and potassium hydroxide, indicating little or no volatile degradation products formed.

After sterilization the membranes were washed and dried. The sulfonated styrene graft on teflon was the only sample which could not be used to construct cells. After drying it became quite brittle and could not be handled without splitting. The remaining four samples were used to build cells. The cells were constructed with standard positive and negative plates and four layers (two layers around each plate) of separator between the positive and negative plates. The unsterilized half of each sample was used to build control cells. The cells were filled with approximately 70 ml of fresh 40% potassium hydroxide and cycled at the three-hour rate. The initial (second cycle) discharge voltage curves for the cells are shown in Figures 3 and 4. The capacity and cycle life data for the cells are shown in Table 4.

Based on the discharge curves and capacities, initially, the acrylic acid and methacrylic acid grafts on teflon gave very good performances, and sterilization did not apparently harm the material. However, cycle life on the teflon cells was not good. The sterilized teflon acrylic acid graft failed after 14 cycles. The control failed after 27 cycles. Both cells failed because of shorts. The sterilized teflon methacrylic acid graft failed after seven cycles and its control failed after 14 cycles. Both of these cells also failed because of shorts, therefore teflon should not be considered as a base material.

All four samples of the crosslinked high density polyethylene (Xlhdpe) material have passed 26 cycles without failing. The sterilized sample of methacrylic acid on Xlhdpe had a discharge curve comparable to the teflons, but the three other samples had discharge curves about 0.05 to 0.10 volt lower indicating the resistance of these materials to be greater.

Based on the cell performance data, it is concluded that the present teflon separators will survive sterilization but will only yield limited cycle life - seven to fourteen cycles. Crosslinked high density polyethylene will survive sterilization and yield better cycle life than the teflon base separator.

Characterization studies on the sample separators involving resistance, exchange capacity, diffusion, etc., have just been completed and will be reported in the next monthly report.

C. Case Material Evaluation

In the previous contract it was found that the nylon case was appreciably attacked by the electrolyte when sterilized at 145°C. There had been very little evidence of attack at 125°C. It was thought that cell failure might be due in part to the degradation products of nylon; therefore, a program was outlined to evaluate various nylons, coatings for nylon, and other high temperature thermoplastics.

1. Nylon

A trip was made to E. I. duPont deNemours and Company in Wilmington, Delaware on June 28, 1963 to discuss the problem of nylon degradation in hot caustic. duPont's representatives could not provide us with any data on the ability of their nylons to withstand attack in potassium hydroxide at 145°C. They suggested that we try Zytel 121, a hydrolysis resistant 6/6 nylon and Zytel 38, a heat resistant 6/10 nylon. We had been using Zytel 101, a general purpose 6/6 nylon. We questioned them about the possibility of "tailor-making" a nylon for our requirements. They stated that little could be gained since the present nylons are the result of years of intensive research, and such a program would be quite costly.

Samples of Zytel 101, 121, and 38 molding pellets were sterilized in stainless steel cans in 40% potassium hydroxide. An adequate quantity of the molding pellets was cooked to assure that it was representative of the surface area of inside the nylon case. The pressures developed in the cans during sterilization are presented in Table 2. The maximum pressures were 38, 35, and 40 psig for Zytel 121, 101, and 38, respectively, which indicates little or no gaseous degradation produced.

The liquor from all three nylon samples contained some suspended material; however, there was no distinguishable odor.

Visual examination of the nylon samples revealed that all three types of nylons were attacked. Zytels 101 and 121 showed the greatest attack. Their surfaces were severely spalled. Zytel 38 showed the least amount of attack. Its surface was only slightly crazed.

Nine cells of standard construction were built. Three cells each were activated with 85 ml of the liquor from each sample of nylon. The cells were formed and cycled at the three-hour discharge rate. All nine cells have passed 54 cycles and are giving performances comparable to the control cells. From this test, it is concluded that nylon degradation products do not impair cell performance.

It is also concluded that Zytel 38 should be used for the case material in preference to Zytel 101 and 121 because it shows the least amount of attack.

2. Coating Materials for Nylon

During our visit to duPont we asked their representative about the possibility of coating nylon with some material to protect it from attack by potassium hydroxide during sterilization. They stated that they did not know of any material to use as it was difficult to get any material to adhere to the surface of nylon.

Although duPont's representatives did not think an impervious coating could be applied to nylon, we decided to check it out experimentally, as outlined in the proposal. After some preliminary experiments, we were able to get what appeared to be good coatings of two different materials (Logo Clear EJ-2741 and Emralon 315) on some nylon test strips.

The coated test strips were sterilized at 145°C for 36 hours in 40% potassium hydroxide. Both materials were stripped from the nylon. No further attempts to coat nylon were made.

3. New Case Materials

Several materials were given consideration for use as possible case materials but only two new materials emerged as possible replacements for nylon. These are Celcon and Penton.

a. Fluorocarbons

Samples of Teflon FEP, Halon TVS, and Kel-F were sterilised in 40% potassium hydroxide at 145°C for 36 hours. None of the samples showed signs of attack or degradation, but all three samples were discolored. Cells were not activated with the liquor from these samples because there was not enough material for an adequate test.

When it became apparent that nylon degradation products were not harmful to cell performance, little additional work was done with the fluorocarbons.

b. Epoxy Molding Compounds

An attempt was made to mold cell cases from epoxy molding compounds, but problems were encountered with the make-shift molding fixtures. Further attempts would have involved obtaining expensive, new molds, so this procedure was dropped.

c. Penton

Penton is a chlorinated polyether manufactured by Hercules Powder Company, Inc. Penton molding pellets were sterilised at 145°C for 36 hours in 40% potassium hydroxide. Examination of the sterilised Penton revealed that there was only a very slight surface attack. The sterilised sample lost its glossy sheen. No distinguishable odor was detected. Three cells of standard construction were activated with 85 ml of the liquor from the sterilized Penton and cycled at the three-hour rate. To date the cells have passed 54 cycles and are comparable to the controls in performance as noted in Table 1.

RE-ORDER No. 63-685

Penton can be injection molded using the same equipment and molds as used for nylon. A sample of a molded Penton case was given to the JPL representatives.

d. Celcon

Celcon is an acetal polymer manufactured by Celanese Chemical Company. It is similar to duPont's Delrin, but according to representatives of the two companies, Celcon has better properties for our application.

Celcon molding pellets were sterilized at 145°C for 36 hours in 45% potassium hydroxide. Visual examination of the sterilized Celcon did not reveal that it was attacked. Three cells of standard construction were activated with 85 ml of the liquor from the sterilized Celcon and cycled at the three-hour rate. To date the cells have passed 54 cycles and are giving performances comparable to the control cells as can be noted in Table 1.

Celcon can also be injection molded with the same equipment and molds as that used for nylon. A case molded of Celcon was also given to the JPL representatives.

III. Seal Investigation

A. Cover-to-Case Seal

Three methods of sealing the case to the cover on nylon were investigated as outlined in the proposal by bonding test strips together and determining the tensile strength of the bond before and after sterilization. Later, prototypes of a proposed new case and cover design were used to evaluate the seals. The phenol seal proved to be best. Heat-sealed cases were also investigated.

Both Celcon and Penton must be heat sealed. Sample cases and covers of the present design were heat sealed, but the seal was inadequate. However, the tests were considered to be inconclusive because the present case and cover is not adequately designed for heat sealing.

RE-ORDER No. 63-695

1. Nylon

Twelve test samples of each seal were prepared. The seals tested were: 88% aqueous solution of phenol; a solution of 10 parts calcium chloride, 22.5 parts nylon, 67.5 parts ethanol; and epoxy (Armstrong A-11). The nylon test strips were cut from molded cases and measured 0.50 wide, 3.125 inches long, and 0.10 inch thick. The strips were overlapped 0.5 inch in making the bond for a total seal area of one-half square inch. A pressure of at least 10 psi was applied to the seal area on strips sealed with phenol and nylon bodied CaCl-Ethanol.

Six samples of each seal were sterilized in stainless steel cans for 36 hours at 145°C in 40% potassium hydroxide. Six samples of each seal were used for controls. The seals were evaluated by clamping the ends of the test strips in the jaws of the tensile machine and subjecting them to a tensile pull along their longitudinal axis.

The results of the tensile tests on the nylon seals are reported in Table 5. The data indicate that the strength of the nylon bodied calcium chloride-ethanol and phenol seals are not appreciably impaired by the sterilization procedure. In most instances, the nylon material broke before the seal. The epoxy seals were weakened by the sterilization procedure and were considerably weaker than the other two seals.

This test data indicated that it should be possible to seal cells by the phenol procedure if pressure could be applied to the seal area during the sealing operation. In order to evaluate this covers were machined from one-half inch thick Zytel 38 stock to fit inside the present case design. The sealing lip on the present case was cut off. The disassembled and assembled case and cover used to evaluate the seals are shown in Figure 5.

All three of the previously described seals and a heat seal were tested with this prototype case and cover. The cover was drilled and tapped to accommodate a pressure gauge or a fitting for attachment to a pressure line. The cells were filled with about 80 ml of 40% potassium hydroxide, supported in stainless steel cans and placed in the oven at 145°C. The maximum pressures developed in the cases were 30 to 32 psig. If the seals survived the thermal treatment, they were checked out at room temperature up to a maximum pressure of 90 psig, after dumping the potassium hydroxide.

Following is a resume of the case-to-cover seal tests:

Phenol Seals

1. Seal OK after 96 hrs at 145°C - OK at R.T. and 60 psi
2. Seal OK after 54 hrs at 145°C - OK at R.T. and 90 psi
3. Seal OK after 54 hrs at 145°C - OK at R.T. and 90 psi
4. Seal OK after 54 hrs at 145°C - OK at R.T. and 90 psi
5. * Seal OK after 54 hrs at 145°C - OK at R.T. and 90 psi
6. * Seal OK after 54 hrs at 145°C - leak at R.T. and 54 psi
7. * Seal OK after 54 hrs at 145°C - leak at R.T. and 30 psi

Epoxy Seals

1. Leak after one hr at 145°C
2. * Leak after two hrs at 145°C
3. * Leak after one hr at 145°C
4. Leak after one hr at 145°C
5. Leak after one hr at 145°C

Nylon Bodied $CaCl_2$ - Ethanol Seal

1. Leak after three hours at 145°C
2. Leak after three hours at 145°C
3. O.K. after 54 hrs at 145°C - Leak at R.T. and 35 psi
4. Leak after one hour at 145°C

Heat Seals

1. Seal broke at 54 psi at R.T.
2. Leak between 2 - 5 hrs at 145°C
3. * Leak between 2 - 5 hrs at 145°C

* Cases molded of glass-filled Z-38

Based on the results of these seal tests, it is concluded that phenol produces the best seal. The seals on cases molded of glass-filled Zytel 38 are somewhat doubtful. The life of the phenol seal is also questionable. One of the phenol sealed cases was inverted so the potassium hydroxide is in constant contact with the seal to test its stand life. Additional tests such as inverting the case during sterilization should be made.

2. New Materials - Celcon and Penton

There is no known solvent seal for either Celcon or Penton, and both materials must be heat sealed. Cases and covers of the present design were molded of Celcon and Penton and were heat sealed using a hot gas technique. The seals held 50 - 60 psig at room temperature but leaked after a few hours at 145°C. The present case and cover are not adequately designed for heat sealing; therefore, the heat seal of Celcon and Penton cannot be properly evaluated until newly designed cases and covers are available for testing.

B. Terminal-to-Cover Seal

The terminal-to-cover seal was evaluated by molding metal pins in test cups to simulate the terminal in the cover. Figure 6 shows a cut-away drawing of the test cup and the actual terminal design. From the figure, it can be seen that the test cup should be more apt to leak than the terminal in the cover.

The test cups were filled with 40% potassium hydroxide and placed in a holding fixture which was attached to a manifold system so five samples could be tested simultaneously. Figures 7 and 8 show test cups, holding fixture, and manifold set up. The test apparatus was attached to an air line and the system was gradually subjected to a total pressure of 90 psig at room temperature. Leaks were detected by swabbing the outside area around the pin with phenophthalein which turned red if a leak occurred. If no leaks were detected, the pressure in the system was reduced to 65 psig, and the apparatus was placed in the oven at 145°C for a minimum of 48 hours.

1. Nylon

Ten Zytel 38 samples were tested and all of them survived the test. Five out of ten glass-filled Zytel 38 samples failed the 90 psig room temperature test, while five survived both tests. It is thought that the reason for failure of these is due to the fact that the glass filler does not allow the nylon to contract tightly around the metal insert. The problem may also be associated with molding techniques and is being investigated further.

2. New Materials - Penton and Celcon

Tests were made on the terminal-to-cover seal for Penton as described above. Five Penton test samples failed to hold electrolyte at 90 psig at room temperature and five samples leaked after two to three hours in the oven at 145°C and 65 psig.

Five Celcon test samples were tested. None of the samples leaked at 90 psig at room temperature, but two samples broke at the flange of the test cup within 24 hours at 145°C and 60 psig. Two of the samples broke at the flange between 30 and 48 hours and one sample survived the test for 48 hours. No leaks were detected at metal-to-plastic seal on any of the samples.

As previously noted, the design inserts in the cover should not be as apt to leak as the straight metal pins in the test cups; therefore, a holding fixture to test the terminal seal in actual covers was designed. Covers molded of Penton and Celcon were tested. No leaks were detected at 90 psig at room temperature. At 145°C and 60 psig the sides of the covers buldged out after a few hours and produced a leak between the cover and the face of the test fixture. The test fixtures are being modified to support the sides of the covers. Figure 9 shows a disassembled and an assembled view of the test fixture. A view of the modified test fixture is also provided. Tests have not been made with the modified fixture at this time.

IV. New Case and Cover Design

The new case and cover designs are illustrated in the sketch in Figure 10 and can be compared to the present case and cover shown in Figure 11. The outside cell dimensions of the new case are about the same as the present cell. The wall thickness of the new case was increased from 0.10 to 0.125 inches for additional strength.

The main feature of the new design is the cover-to-case seal area as it has three advantages over the present design. One is that it is more applicable to a heat seal which will be necessary if either Celcon or Penton is used as a case material. The second advantage is that pressure can be applied to the seal area between the case and cover. When pressure is applied to the seal area of the present design, the walls of the case bow in where the cover overlaps the case, consequently, very little pressure is actually applied between the cover and the case. The third is that there are no weak spots due to shoulders and ledges in the new case such as there are in the present case. As can be noted in Figure 11, the wall thickness of the case at the seal area is only about half that of the body of the case. In addition it will be noted that there is a detent or notch molded in the side of the case at the seal area to provide a snap fit of the case and cover. At these notches the wall thickness is only about 0.01 inch and has been a source of failure. During the previous investigation most of the leaks occurred at the cover-to-case seal due either to poor seals or cracks in the case. It is felt that the new design should alleviate this problem.

The terminal-to-cover seal was not changed since past experience has proven it to be quite adequate. Molds for the new case are under construction and should be completed the first or second week of December.

V. Conclusions and Recommendations

Unformed positive plates survive sterilization without detrimental effects. Unformed negative plates survive sterilization without detrimental effects; however, abnormal pressures are produced during sterilization. The pressure problem is associated with the polyvinyl alcohol binder and the viscon paper wrap. The PVA binder can be eliminated without serious loss in cycle life, and it might be possible to substitute one of the new separator materials for the viscon paper.

The fibrous sausage casing separator materials must be replaced. Dynel is degraded beyond use and causes loss of divalent silver-oxide voltage on discharge. Fibrous sausage casing is severely degraded and its degradation products cause immediate cell failure. Permion 600 is not degraded as severely

RE-ORDER No. 63-685

as Dynel or F.S.C., but its degradation products cause early cell failure, probably because it is a cellulosic type material.

Degradation products from the three nylons tested do not seem to affect cell performance. Zytels 101 and 121 are more severely attacked by hot potassium hydroxide than Zytel 38. Preliminary work indicates that Zytel 38 can be used as a case material and is the best selection of the nylons.

Two other possible case materials, Penton and Celcon, were found which are not appreciably attacked during sterilization, and their degradation products do not affect cell performance. Both materials can be molded with the same molds and equipment as used for nylon. Both materials must be heat sealed. The cover-to-case seal cannot be properly evaluated until the new cases and covers are available for testing. The terminal-to-cover seal evaluation has not been completed and remains in doubt.

Of the four methods of sealing nylon investigated, phenol produces the best seal, but its service life is questionable. Sealing glass-filled Zytel 38 has not been successful and continued evaluation is recommended. Four of the five new separator materials supplied by Radiation Applications Incorporated survived sterilization. Sterilized teflon base separators with acrylic and methacrylic acid grafts failed after seven to seventeen cycles because of shorts. It is thought that the shorts are due to small holes inherent in the teflon films during manufacture. The sterilized crosslinked high density polyethylene separators must be concluded to be the best since they have passed 26 cycles without failure.

Since the chief cause of cell failure has been traced to the separators and new separator materials have been found, it is recommended that the program be continued. Utilizing the proposed new case and cover design and R.A.I. separators, it should be possible to build cells which will survive the 145°C sterilization requirement. The cycle life is expected to be as good as that of the crosslinked high density polyethylene separators which have passed 26 cycles. Both the methacrylic and acrylic acid grafts on crosslinked high density polyethylene membranes should be tried in the next phase of the program.

RE-ORDER No. 63-6??

TABLE 1

Capacities of Various Cell Groups - Ampere Hours

Cycle		5*	10	15	20	25	30	35	40	45	50	54
Dynel	1	23.5	24	24.2	23.6	22.8	24.3	28.3	26.9	25.8	23.1	23.1
	2	26.0	28.5	28.7	28.1	26.8	26.2	30.0	28.2	26.7	25.5	24.3
	3	27.0	27.5	26.9	26.6	25.0	26.2	27.7	29.2	27.6	25.5	24.9
Penton	1	24	24	21.8	22.4	23.1	23.7	23.2	22.2	22.5	21.6	21.0
	2	26	26	22.5	23.1	23.7	22.8	23.2	22.5	22.2	21.6	21.6
	3	23.5	23.5	22.2	23.1	23.8	22.7	23.0	23.4	23.4	22.6	22.7
Z-101	1	26	28	28.0	29.1	28.8	28.6	29.0	28.2	28.5	28.4	28.6
	2	23	23	19.4	20.4	21.9	21.8	22.8	21.7	21.6	21.6	20.9
	3	24	27	23.4	23.7	24.0	22.8	22.8	22.2	21.9	21.6	21.8
Z-121	1	18	23	17.2	19.8	20.6	20.8	19.8	19.2	18.5	19.1	16.8
	2	22.5	24.5	21.8	19.8	19.9	21.3	20.1	19.2	18.8	16.8	13.6
	3	27	26	24.5	25.5	25.8	26.0	26.3	25.6	25.5	25.0	24.6
Control	1	24.5	25.5	24.2	25.1	24.7	25.4	25.5	25.2	26.1	26.9	26.4
	2	24.5	25	23.0	23.6	24.6	23.9	25.5	24.7	25.2	26.9	26.0
	3	19	20	17.0	19.4	19.8	20.8	24.3	23.1	23.3	24.3	23.7
P-600	1	21	22.5	20.4	20.6	21.8	removed from test after cycle 27					
	2	18.5	20	15.7	14.4	9.5						
	3	18.5	19	15.4	15.8	13.6						
Celcon	1	24.5	25.5	22.8	22.5	22.5	22.5	23.8	23.6	23.2	21.5	22.4
	2	24	25	22.0	20.0	19.5	20.1	21.6	19.8	21.0	21.0	21.0
	3	27	28.5	25.9	26.8	26.6	26.8	27.5	27.7	27.9	29.0	28.4
Z-38	1	25.5	26	28.4	27.5	27.9	27.9	27.9	28.4	29.8	28.5	28.4
	2	25.5	23	24.6	24.3	25.0	25.7	27.6	26.7	27.0	27.6	27.8
	3	26	25	25.6	26.1	25.9	26.4	27.3	27.5	27.0	27.6	27.8
T.S.Neg.	1	22.5	26.5	27.6	27.4	27.2	25.4	26.9	26.2	29.2		
	2	21.0	23.5	22.6	24.1	22.2	20.6	20.6	22.7	23.6		
	3	23	26.	26.6	25.8	26.0	24.0	24.3	26.4	28.4		
T.S.Pos.	1	24.5	25	26.6	26.7	27.6	29.9	29.4	30.0	30.8		
	2	22.5	23.5	26.0	25.5	25.2	27.9	26.9	27.9	28.8		
	3	24.5	25	25.2	25.8	26.4	28.8	27.1	28.2	29.7		
T.S.Neg.	1	22	22	24.9	26.8	25.2	24.2	25.5				
No PVA	2	24.3	24.2	28.0	29.0	27.3	26.0	27.3				
	3	22.2	23.7	27.6	23.8	27.3	26.2	26.4				
ZnO-HgO	1	23.3	23.8	27.8	26.1	24.5	22.5	23.4				
Mix	2	24.6	25.6	29.2	27.6	27.2	25.5	27.0				
	3	21.6	23.2	29.2	28.4	26.8	24.8	26.1				

Every fifth cycle reported. Intermediate cycles omitted for sake of brevity.

* After nine day activated stand

RE-ORDER No. 63-685

TABLE 2

Pressures Developed by Components During Sterilization

Hours	FSC	Zytel 101	Zytel 121	Zytel 38	Dynel	Permion 600	Celcon	Penton	Pos. Plates	Neg. Plates	Neg. Plates without PVA	Neg. Plate Material ZnO-2% HgO Only
1	21	26	24	32	26	30	28	32	16	24	28	22
2	36	34	30	34	40	42	33	32	29	50		
3	40	34	33	36	49	44	36	34	32	66	45	30
4	-	34	33	36	-	-	36	34	32	72	47	32
5	42	34	36	36	51	46	40	40	34	80		
6	42	34	36	36	52	47	40	40	34	86	45	31
7	42	34	36	36	54	48	40	40	34	89	50	32
8	44	34	36	36	54	48	40	40	34	89		
9	-	34	36	36	-	-	40	-	-	90	53	32
24	52	34	36	38	55	56	40	40	34	100+	60	30
30	54	35	-	-	55	-	-					
36	54	35	38	40	55	57	40	42	36	100+	62	30
Room Temp.	7	0	0	0	3	6	0	0	0	40	13	0

22

RE-ORDER No. 63-683

TABLE 3

Pressures Developed by RAI Separators During Sterilization

	XLHDPE acrylic acid graft	XLHDPE methacrylic acid graft	Teflon methacrylic acid graft	Teflon sulfonated styrene graft	Teflon acrylic acid graft
1	22	24	28	25	25
2	26	29	34	28	32
3	26	30	35	31	33
4	26	30	35	30	34
5	26	30	35	29	31
8	26	30	35	29	33
9	26	30	35	29	32
24	25	29	36	28	32
28	22	29	38	28	32
30	21	29	38	28	
36	20	29	38	28	31
Room Temp.	0	0	0	0	0

23

TABLE 4

Cycle and Capacity Data - Cells with RAI Separators

Ampere Hours

Cycle	1	2	3	4	5	6	7	8	9	10	11	12	13
AA on Teflon Control	28	28.5	29	27	27	30.4	29.1	30.6	30.4	31.8	30.4	30	29.9
AA on Teflon Sterilized	32	29.6	29	30	30	31	32	32	30	31	31	31	31
AA on Xlhdpe Control	20	25	26	23.2	24.5	22.6	22.2	22.0	21.3	22.0	20.1	20.2	19.5
AA on Xlhdpe Sterilized	22.5	26.9	28.0	26.3	28.0	28.6	26.8	26.2	24.7	24.2	24.0	22.3	22.8
MAA on Xlhdpe Control	22.6	27.2	28.5	27.6	29.4	27.4	27.2	26.5	24.8	25.3	24.0	22.8	23.0
MAA on Xlhdpe Sterilized	30	29.8	29.9	29.3	32.4	33	28.2	31.9	31.2	30.2	30.4	33.8	30.7
MAA on Teflon Control	26.8	29.3	28.8	27.4	29.4	27.3	27	26	25.8	26.1	26.1	24.9	25.4
MAA on Teflon Sterilized	30.8	33.0	31.2	29	30.7	20.7	20.8	removed from test - shorted 10-10-63					
Sulfonated Styrene-Teflon	19.5	26.9	27.2	25.4	27.9	26.4	26	26.5	25.8	25.5	24.8	23.4	23

24

TABLE 4 (Continued)

Cycle and Capacity Date - Cells with RAI Separators

Ampere Hours

Cycle	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28
AA on Teflon Control	29.6	28.6	27.3	27.7	22.5	24.9	24.9	23		19.2	18.5	18.	7.3	9	2
AA on Teflon Sterilized	30.8	removed from test - shorted 10-7-63													
AA on Xlhdpe Control	19.4	19.6	19.5	18.5	18	19.2	18	14.8	17	16.5	13.5	14.4	14.4		
AA on Xlhdpe Sterilized	22.2	22.2	21.4	20.1	21.4	19.2	18	16.1	17.4	17.7	17.4	19	17.1		
MAA on Xlhdpe Control	22.3	24.2	23.6	21.6	22.5	23	22.5	19.1	19.5	21.2	20.6	21.4	19.6		
MAA on Xlhdpe Sterilized	30.7	31	30.7	30.7	31.5	31.5	27	30.1	31.5	31.2	31.3	26.8	30.8		
MAA on Teflon Control	24.9	5.2	removed from test 10-23-63												
MAA on Teflon Sterilized	removed from test														
Sulfonated Styrene-Teflon	22.5	23.6	23.4	21.6	21.4	21	20.4	18.6	19.1	19.7	18.4	19.5	17.6		

RE-ORDER No. 63-675

TABLE 5

Tensile Test Data Nylon Seals

Controls

Data Recorded in Pounds Pull

$CaCl_2$-Ethanol	Phenol	Epoxy
120	226 *	104.5
144	55	80
121	405 *	77
165	279 *	248
163	353 *	139
150	250 *	95
Samples Sterilized at 145°C for 36 Hours in 40% KOH		
167 *	180 *	0
211 *	187 *	56
174 *	270 *	74
128 *	244 *	59
129 *	136 *	52
70	140 *	70

* Material broke before seals

The nylon test strips were cut from molded cases.

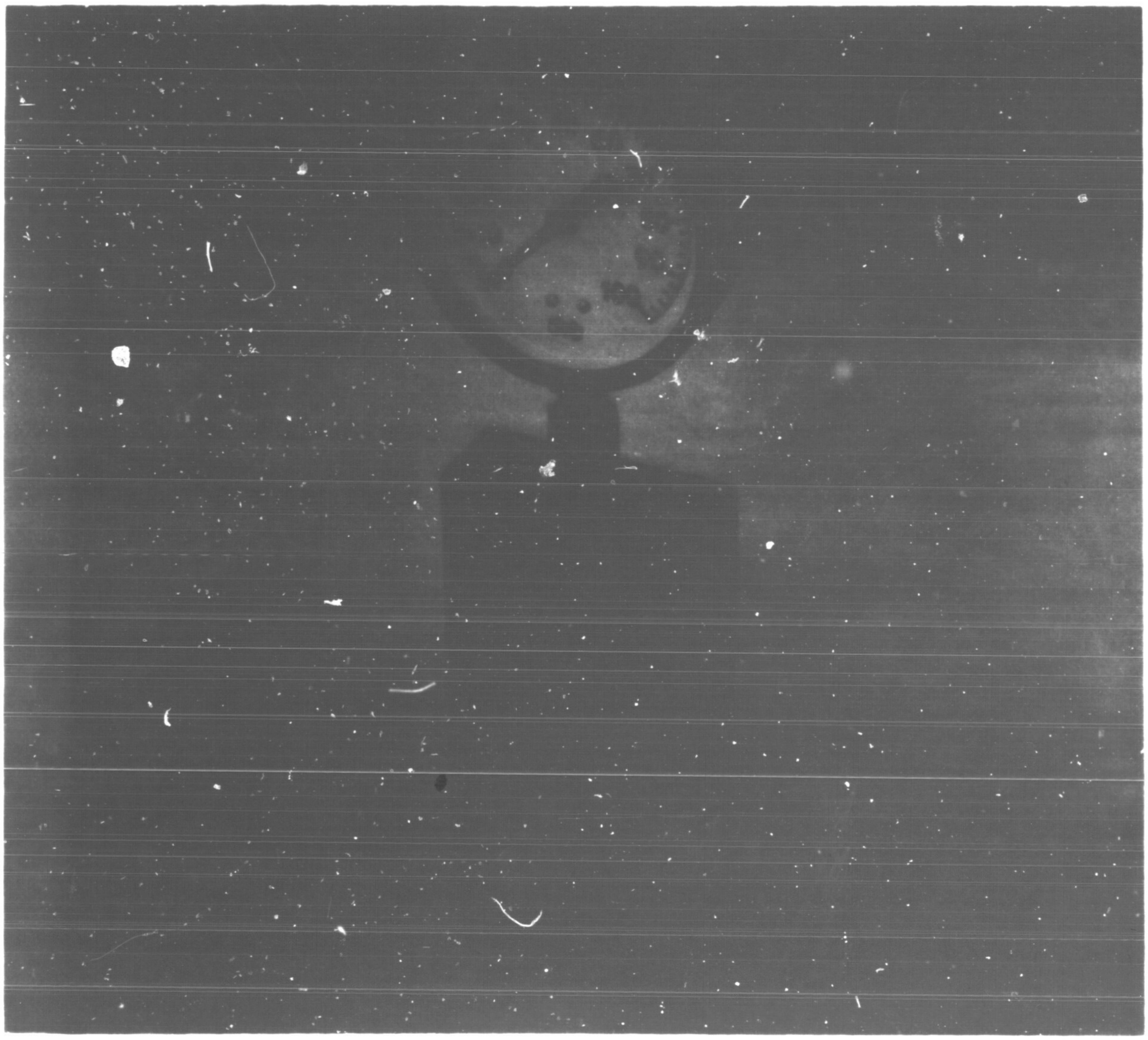
The strips were 3-1/8 inches long, 1/2 inch wide, and 1/10 inch thick.

The seals were made by overlapping the strips 1/2 inch.

26

FIGURE 1

Stainless Steel Sterilization Container



RE-ORDER No. 63-685

FIGURE 2

Typical Discharge Curves at 9 Amperes R.T.

Each Group is Average of 3 Cells

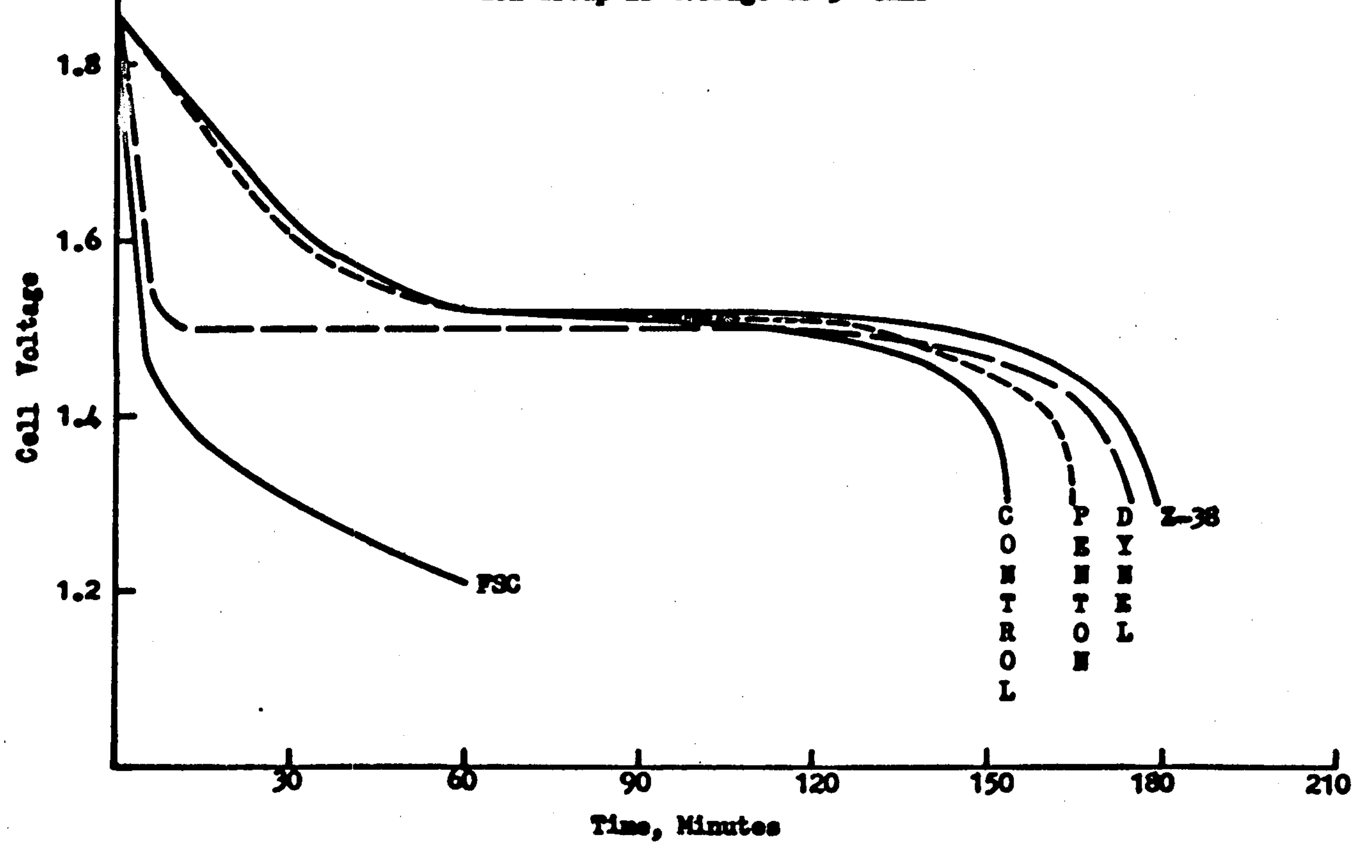


FIGURE 3

Discharge Curves of Cells Built with R.A.I. Separators (9 amp. at R.T. 2nd Cycle)

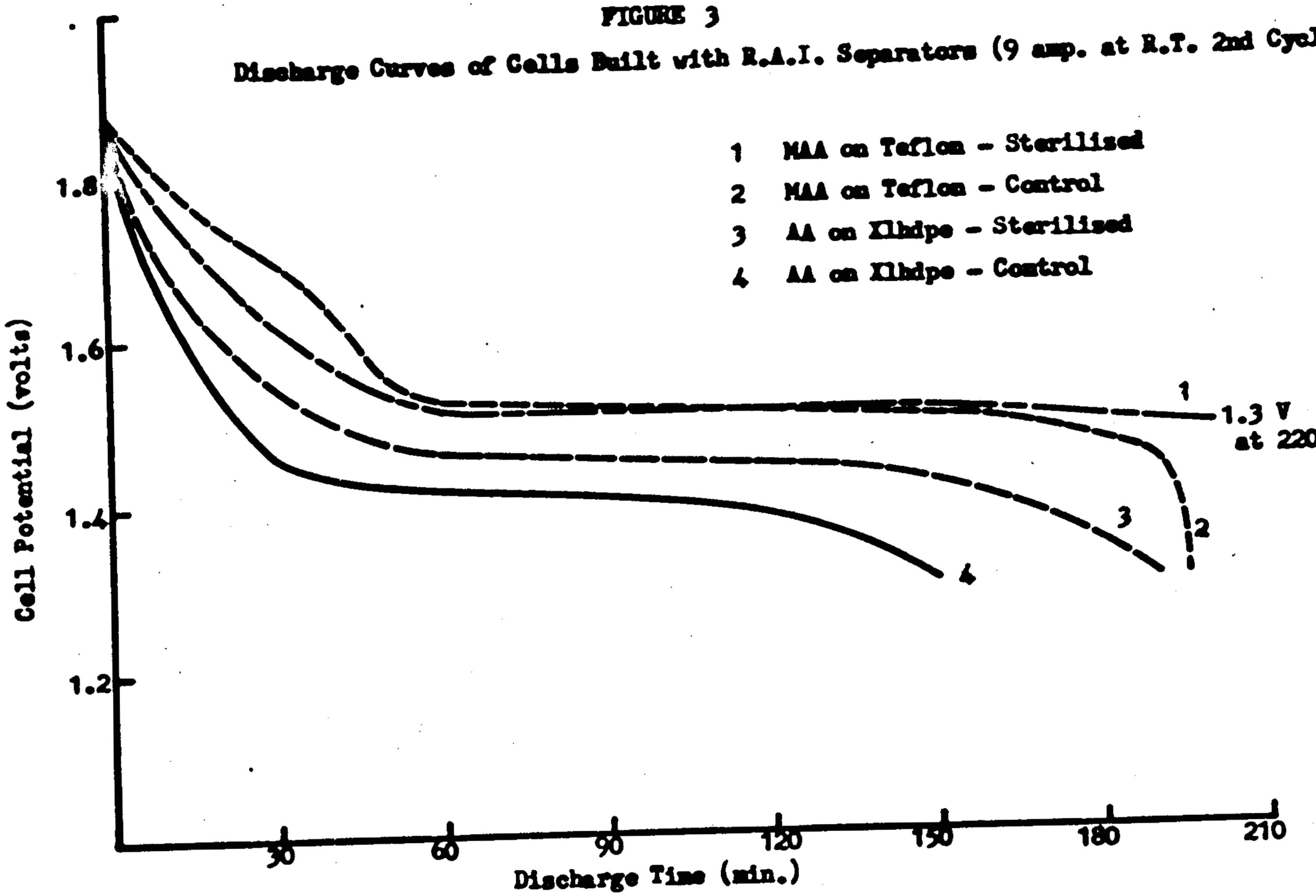


FIGURE 4

Discharge Curves of Cells Built with R.A.I. Separators (9 amp. at R.T. 2nd cycle)

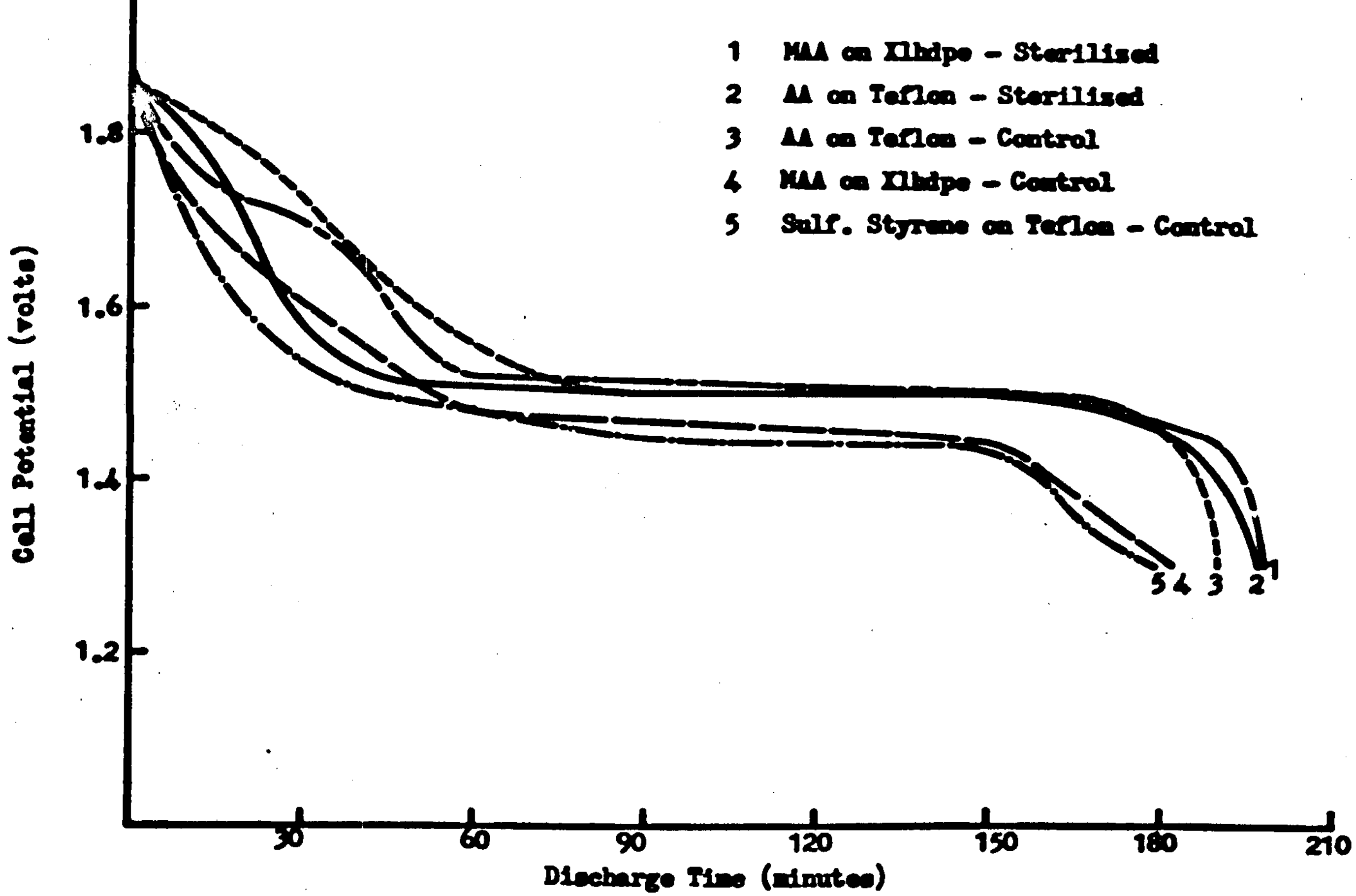


FIGURE 5

Prototype Case and Cover For Seal Evaluation

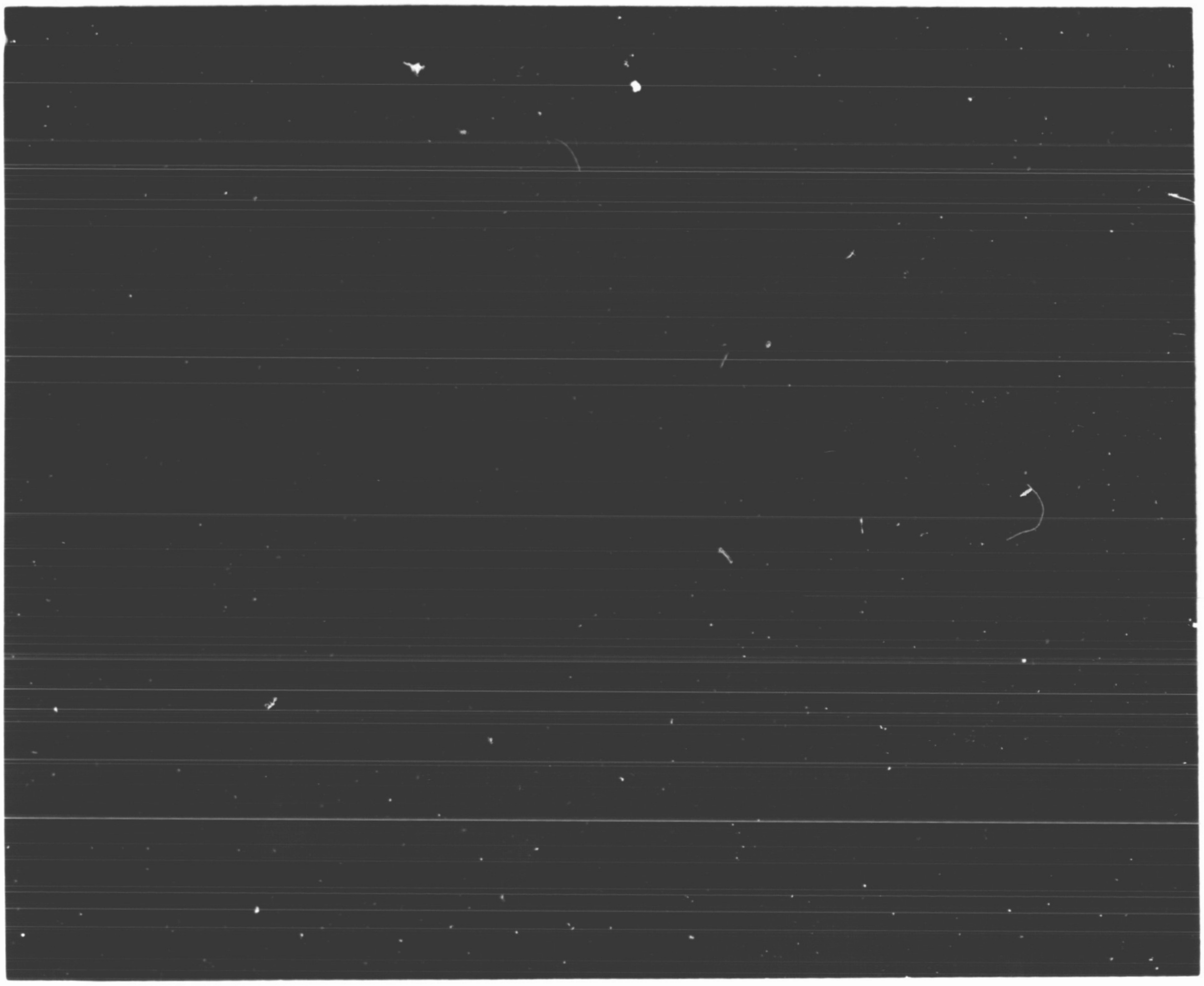
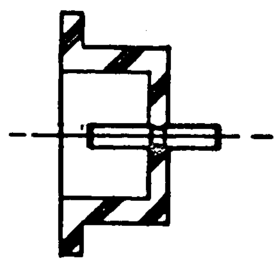
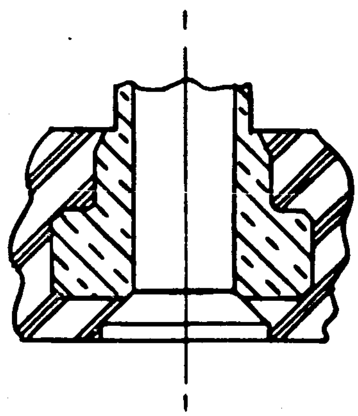


FIGURE 6

Cross Section of Test Cup and Terminal Design



Cross section of insert-test cup



Cross section of terminal in cover

FIGURE 7

Test Cup and Holding Fixture

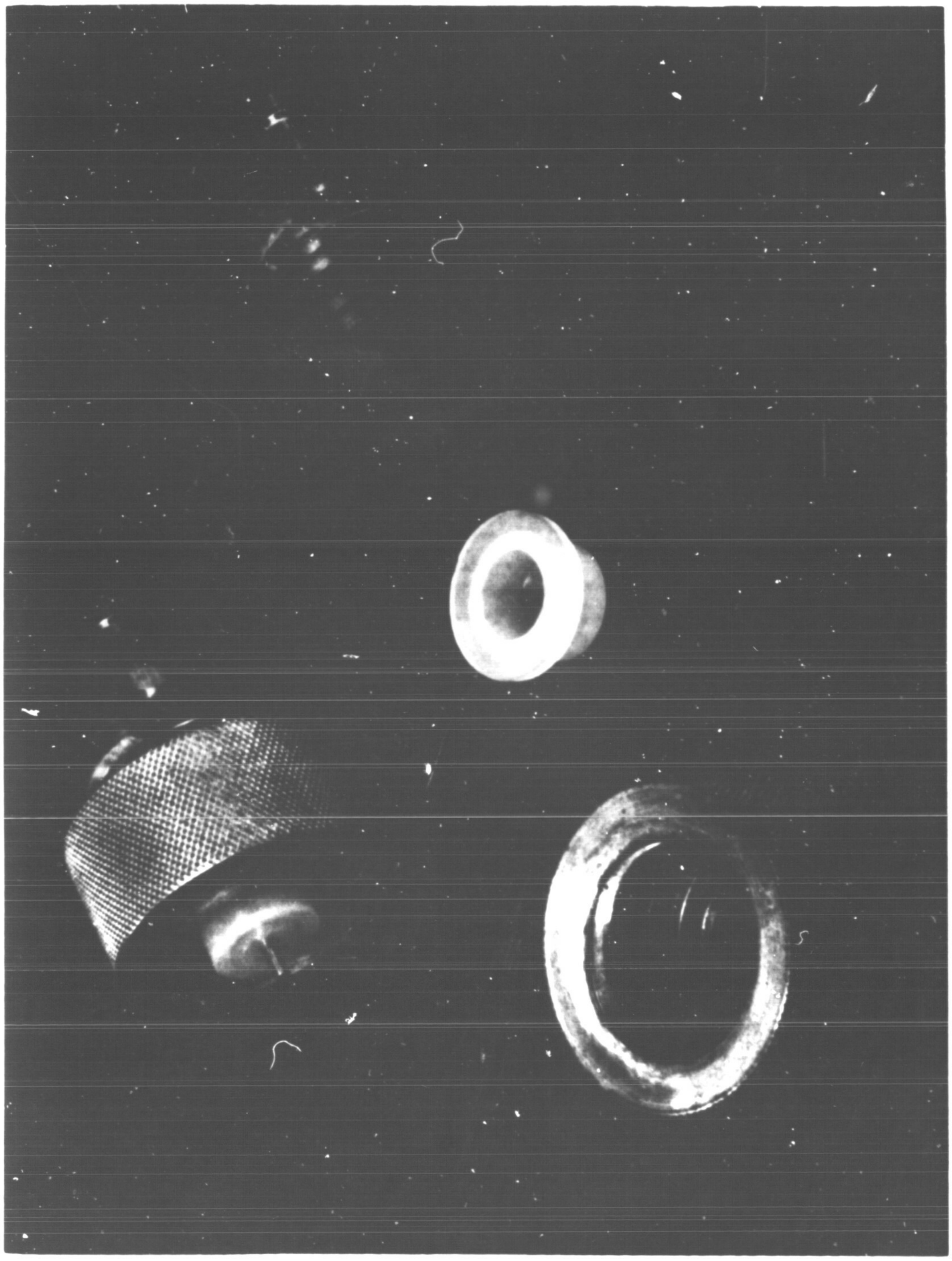


FIGURE 8

Apparatus For Terminal-to-Cover Seal Evaluation

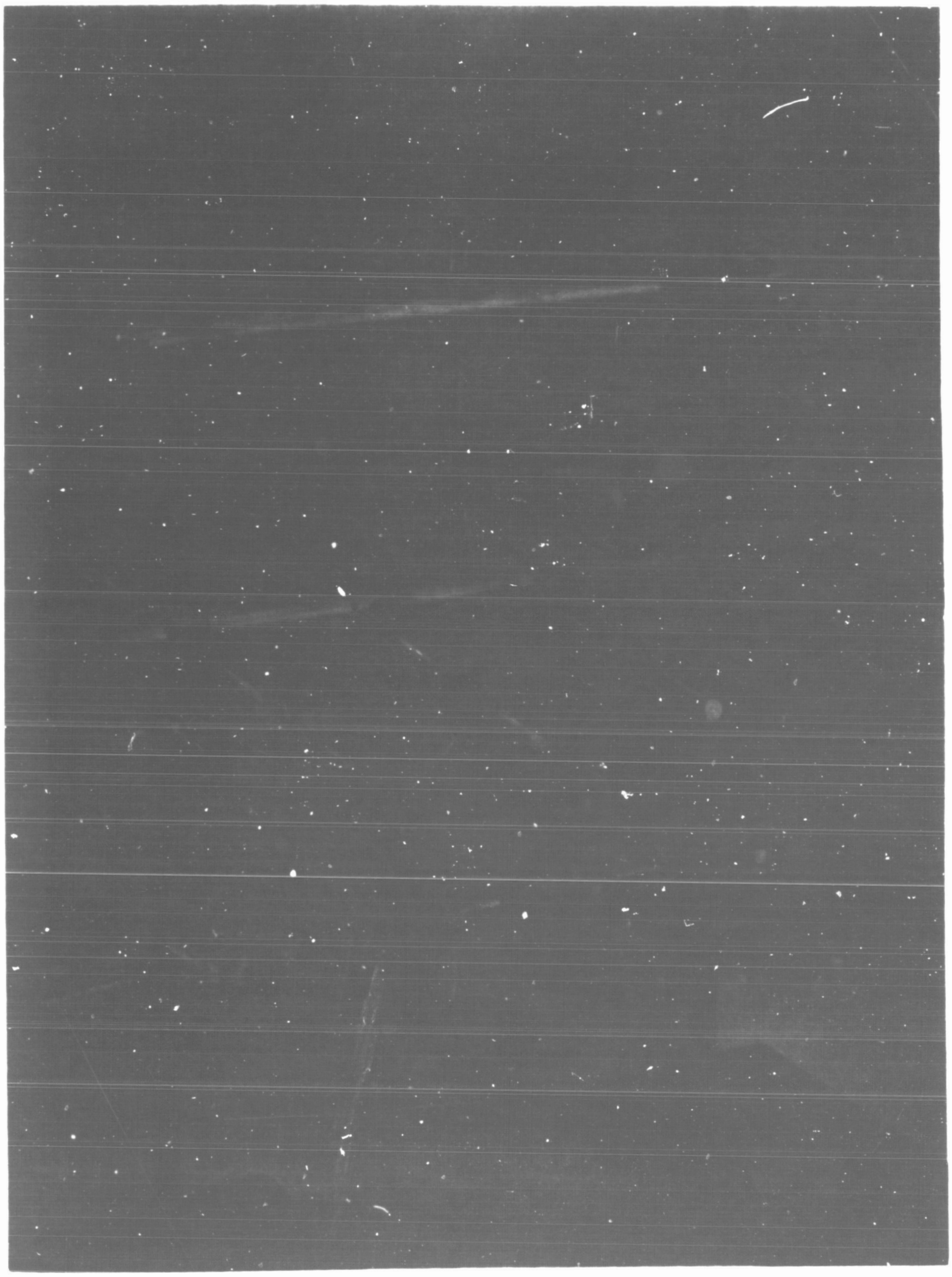


FIGURE 9

Cover and Holding Fixtures - Terminal Seal

RE-ORDER No.

FIGURE 10

New Cell Design

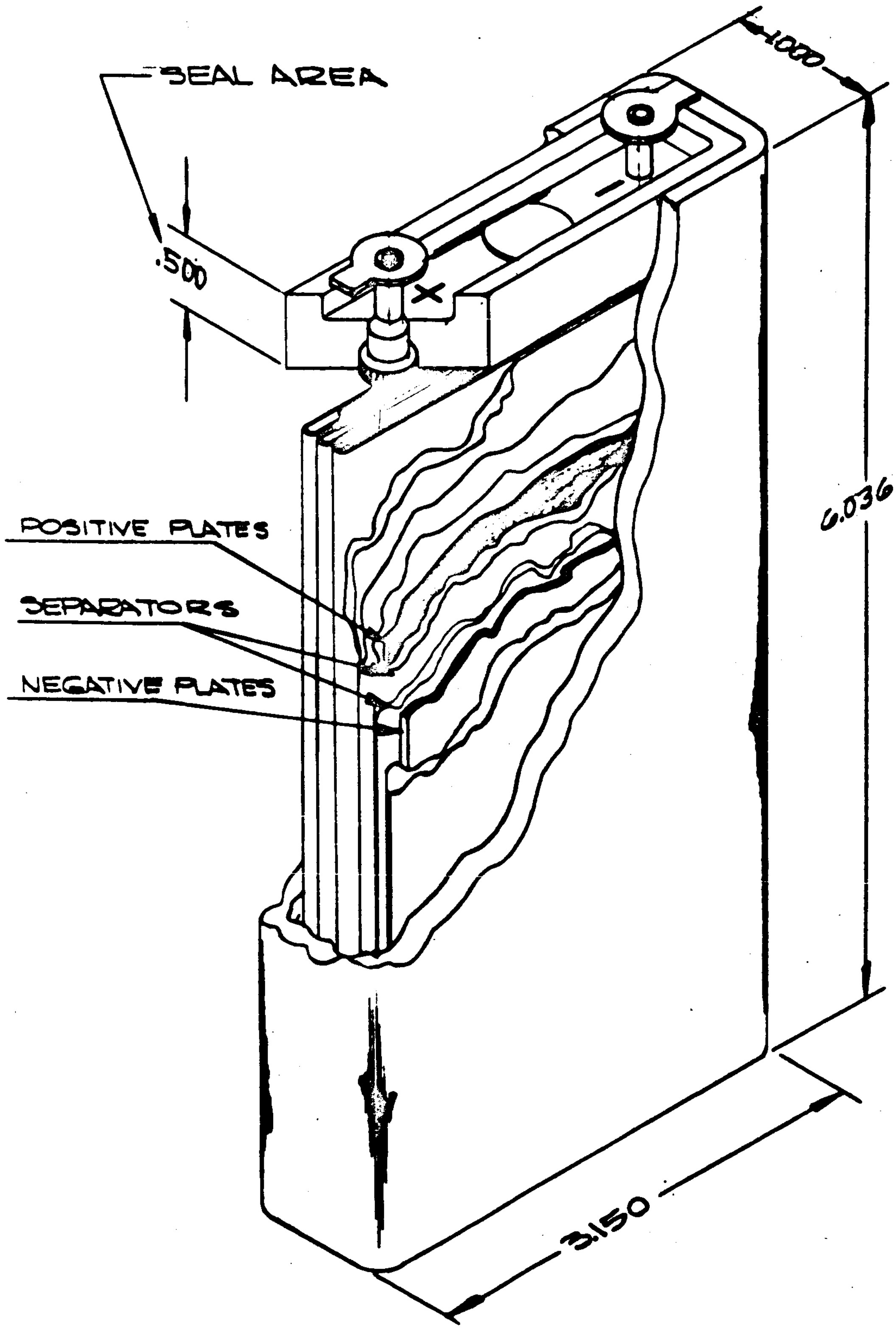


FIGURE 11

Present Case and Cover